X-Ray Studies of Fatty Acids and Mixtures of Fatty Acids

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

FRED B. SLAGLE

Baltimore, 1933

[Reprint from the Journal of the American Chemical Society, **55**, 4396 (1933).]

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ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Emil Ott for suggesting this problem and for his continual assistance and encouragement during the course of the work.

He also wishes to thank Dr. E. E. Reid, Dr. Jane Meyer and Dr. John Ruhoff for supplying the pure saturated fatty acids, C_{10} to C_{18} inclusive, which were used in this research.

The author is also indebted to the other members of the Chemistry Staff for much inspiration and aid received in classroom and laboratory.

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X-RAY STUDIES OF FATTY ACIDS[1]

Introduction

The long spacings of normal fatty acids have been measured by a series of investigators.[2] However, most of this work is not reliable, due in part to insufficient purity of the acids used. Due to the fact that we had a series of acids of exceptional purity available, it seemed worth while to repeat such measurements with increased accuracy. This was especially desirable in view of the study of mixtures of such acids which will be reported in a following paper.

Experimental Procedure

A. Spectrograph.—In all the work reported here a Bragg spectrograph (made in the Seeman Laboratory, Freiburg, i. Br.) with the approximate radius of 16.79 cm. was used. The adjustable front slit was set at 0.1 mm. during all of this work. Most of the measurements of the fatty acids were made by rotating the crystal at constant speed through the angle from 0 to $\pm 10°$, since we were only interested in the lower order reflections. The reflections were registered on Eastman x-ray films.

B. x-Ray Source.—x-Rays were obtained from a Seeman metal tube, using a tungsten filament and a copper target, the operating peak voltage being 40 kilovolts at 20 milliamperes. A nickel filter of 0.02 mm. thickness was used over the window of the tube at all times to cut out the β-radiation from the copper. The target of the tube was periodically cleaned, thus avoiding tungsten radiation, which under the worst conditions was found by spectrographic measurements to be less intense than the β-radiation from the copper after passing through the nickel filter. The β-radiation was never observed for the fatty acid reflections.

(1) Emil Ott and F. B. Slagle, compare preliminary note, *J. Phys. Chem.*, **37**, 257 (1933).

(2) Compare P. P. Ewald and C. Hermann, "Strukturbericht (1913–1928)," Akademische Verlagsgesellschaft, Leipzig, 1931, pp. 691–700.

C. Calibration of the Spectrograph.—Since the spectrograph was built with moderate precision only, it was found necessary to calibrate the instrument with utmost care in the angular range of the contemplated measurements. The reflections from mica do not completely cover this range when copper radiation is used, but the use of silver radiation eliminates this difficulty. It was found advisable to standardize the mica used against calcite, instead of using the mica values given by Siegbahn.[3] Actually we found appreciable deviation, which is to be expected in view of the chemical variations in mica. The fact that various micas have different c-spacings is also borne out by the work of Rinne[4] and Mauguin.[5]

The calibration of the spectrograph was then accomplished as follows. The first order reflection from the rhombohedral face of pure calcite (obtained from Dr. W. M. Thornton, Jr., of this Laboratory) is registered on a photographic film. The distance L between the corresponding reflections on either side of the primary beam is measured with a microcomparator to 0.01 mm. A correction for film shrinkage is obtained by imprinting on the undeveloped film in various places two points of known distance apart. This mode of measurement is applied in all cases. The third-order reflection of mica falls very close to the observed calcite reflection (Cu-radiation is used), and thus permits an accurate determination of the observed glancing angle Θ. From this third-order reflection, the other orders of mica are calculated according to Bragg's law. It is now possible to plot Θ against L. To obtain further calibration points the various reflections of mica are also obtained with silver radiation. We are thus enabled to obtain the Θ values of unknown substances by measurement of their L values.

The exact calculations of Θ used in this calibration should be given. The ordinary Bragg equation, $n\lambda = 2d \sin \Theta$ does not apply exactly when the index of refraction differs from unity. The corrected equation takes the form[3]

$$n\lambda = 2d\left(1 - \frac{4d^2}{n^2}\frac{\delta}{\lambda^2}\right)\sin\Theta$$

Siegbahn[3] gives the values of d from the rhombohedral face for calcite as calculated from the various orders, and it is observed that d becomes larger for the higher orders and approaches a constant value. The observed value for the first-order reflection of calcite is given as $d_1 = 3.02904$ Å.[3] From the ordinary Bragg's law ($n\lambda = 2d \sin \Theta$) we obtain the value of Θ for this first-order reflection. From the measurement of L, the effective radius, r, in the vicinity of the reflection is calculated. This value of r will be applicable to the third-order reflection of mica. Thus d_3 for mica is determined as 9.93447 Å. Knowing $\delta/\lambda^2 = 3.86 \times 10^{-6}$,[3] the true spacing d may be determined as follows

$$\text{since } d_n = d\left(1 - \frac{4d^2}{n^2}\frac{\delta}{\lambda^2}\right), \text{ it follows}$$

$$9.93447 = d\,(1 - (4d^2/9) \times 3.86 \times 10^{-6}) \text{ or}$$

$$d = 9.93615 \text{ Å}.$$

The value for any d_n may now be calculated, and by use of the ordinary Bragg's law again, the values of Θ may be calculated for any order and used in the calibration. Thus we obtain a plot of true angles against L.

(3) Manne Siegbahn, "Spektroskopie der Röntgenstrahlen," Verlag Julius Springer, Berlin, 1931.
(4) F. Rinne, *Z. Krist.*, **59**, 230 (1924).
(5) Ch. Mauguin, *Compt. rend.*, **186**, 879, 1131 (1928).

This calibration curve is used in the determination of the Θ values of the fatty acids. For the calculation of the *d* values, the corrected Bragg formula should be used (δ/λ^2 is not known). However, it is found that within the limits of the accuracy of the determinations, no systematic deviations are found when the ordinary Bragg's law is applied.

In cases with sharp lines the agreement for different orders is within one-tenth of one per cent. This accuracy is reproducible with different mountings of the sample, as well as with different chemical preparations. With broadened lines the accuracy is within five-tenths of one per cent. This precision appears to be higher than any previously obtained.

The values of the wave lengths used throughout this work are those given by Siegbahn.[3]

D. Measurement of Films.—On all of the pictures obtained from the fatty acids there were some strong lines (odd orders), and some weak lines (even orders). The accuracy of measurement of these lines depends on their strength and their sharpness. The strong, well-defined lines were measured with a microcomparator and the measurements could be checked to 0.01 mm. The weak lines were measured with a millimeter scale. The lines of intermediate strength were measured with either the microcomparator or the scale, depending upon the individual case.

In order to obtain the best value for each line, a series of measurements was taken on that line and the average value so obtained reported. All of the measurements of lines given in the tables to follow will be such average values. Those measurements which were made with the microcomparator will be marked (com.). All other lines were measured with the millimeter scale.

E. Preparation of Samples.—A short description of the three methods of preparing the samples is as follows:

(a) **Crystallization from Acetone.**—A few drops of an acetone solution of the pure acid were put on a glass plate and the acetone allowed to evaporate off. By regulating the rate of evaporation and the concentration of the acetone solution, it is very easy to obtain a uniform deposit on the plate of about 0.1 mm. in thickness.

(b) **Melting on Glass Plate.**—The technique for preparing samples by this method was more difficult. If a small amount of the acid is melted on a glass plate, it will persistently form a drop and not spread over the surface of the glass. If enough of the material is used a layer of the acid can be formed on the glass plate upon cooling, but such a layer will be very thick (about 1.0 mm.) and show very poor orientation. It was found necessary to form a much thinner film on the plate, causing longer exposure time. By spreading a small drop of the acid over the surface of the glass plate, and cooling rather rapidly (to avoid coalescence to a single drop) such thin films, of practically uniform thickness, can be deposited.

(c) **Pressing of Solid Sample on Glass Plate.**—If sufficient pressure is exerted upon a solid fatty acid it can be made to adhere to a glass plate. By pressing the acid between two glass plates it was found that the sample would spread to a uniform thickness. If the sample thus formed is thin, one of the glass plates can be removed so that all of the acid will remain in a thin film on the other glass plate. Samples prepared by this method are somewhat thicker than those prepared by the other methods and the reflection lines obtained are broadened.

F. Source of Acids.—The acids, C_{10} to C_{18}, used in this research were prepared by Dr. J. D. Meyer[6] and Dr. John Ruhoff under the direction of Prof. E. E. Reid. The

(6) J. D. Meyer and E. E. Reid, *J. Am. Chem. Soc.*, **55**, 1574 (1933).

methods of preparation and purification are given in detail in dissertations submitted by them to the Johns Hopkins University in 1932. In addition the C_{19} acid was prepared by the author according to the same methods.

It is believed that the purity of these acids is 99.5% or better (judging from the cooling curves which were obtained), which appears to be purer than the acids used by the other investigators in this field.

G. x-Ray Measurements on the Pure Acids.—The pure acids ranging from C_{10} to C_{19} have been studied with samples prepared by the three methods given previously. All these pictures were taken at room temperature (23 to 28°) excepting for C_{10} and C_{11} which, due to their low melting points, were taken at a slightly lower temperature (20 to 22°) in order to be sure that the sample remained solid during the exposure. The effect of this temperature variation upon the spacing of the (001) planes is easily within experimental error. In the case of the hydrocarbons, Müller[7] found that the expansion along the *c*-axis between liquid air temperatures and room temperatures was so small as to be unmeasurable. Dr. D. A. Wilson of this Laboratory has, in the case of C_{15} acid, observed a slight variation in the spacing between −50 and +25°. This sample, which was prepared by crystallization from acetone, gave a spacing of 35.63 ± 0.05 Å. at 25°,

TABLE I

The letter A, B, C or D before each value stands for the modification as listed by Francis, Piper and Malkin. The values marked (*) will be explained in the discussion. The setting points given above are taken from the dissertation of Dr. J. D. Meyer, excepting for C_{19} which was determined by the author. Cooling curves for these acids are also given by Dr. Meyer.

Acid	Setting points	Melted	Acetone	Pressed	Piper's values
C_{10}	31.19	(C)23.02	(C)23.02	(C)22.95	.....
C_{11}	27.77	(C)25.32	(C)25.40	(C)25.22	.....
C_{12}	43.22	(C)27.18	(C)27.18	(C)27.31	(C)27.4
C_{13}	41.55	(A)34.92	(A)34.92	(A)34.84	(A)35.3
		(B)31.27			(B)31.65
C_{14}	53.86	(C)31.44	(C)31.39	(C)31.26	.....
				36.64	
C_{15}	52.26	(B)35.75	(B)35.63	(B)35.67	(B)35.8
		(A)39.88			(A)40.0
C_{16}	61.82	(C)35.52	(C)35.47	(C)35.53	(C)35.65
			(B)39.35		(B)39.1
C_{17}	60.66	(C)38.57	(B)39.98	(B)40.05	(B)40.5
				(D)32.85	(D)33.9
				(A)44.42	(C)38.6
C_{18}	68.82	(C)39.83	(C)39.62	(C)39.92	(C)39.95
			(B)44.14	(B)44.14	(B)44.0
			(A)46.15	(A)46.29	(A)46.6
C_{19}	67.64	.....	(B)44.13	(B)44.37*	(B)44.5
				(B)44.14*	

(7) A. Müller, *Proc. Roy. Soc.* (London), **A127**, 417 (1930).

and a spacing of 35.19 ± 0.10 Å. at −50°. This change in spacing of 0.44 Å. corresponds to a temperature change of 75°, or a change of 0.00587 Å. per degree.

Table I gives the best value for the spacings obtained by the three methods of preparation together with the corresponding values reported by Francis, Piper and Malkin[8] and the setting points of the acids. Fig. 1 gives the plot of the spacings obtained for the pure fatty acids.

The following typical results will demonstrate the check obtained for the spacing from the successive orders (starting with the first order).

	C_{16} Acid melted on glass plate $\sin\theta/n$	C_{13} Acid crystallized from acetone on glass plate $\sin\theta/n$	C_{12} Acid pressed on glass plate $\sin\theta/n$
	0.02167 (com)	0.02204 (com)	0.02815 (com)
	.02167 (com)	.02204	.02814
	.02166 (com)	.02203 (com)	.02819 (com)
	.02162 (wk)	.02202	.02817
	.02165 (com)		
	.02164		
Average	.02166	.02203	.02816
d	35.52 Å.	34.92 Å.	27.32 Å.

(com) = comparator measurement. (wk) = weak line.

A check was made on several acids to see how reproducible the results were. The samples were crystallized again on a glass plate, using the same method of crystallization and the sample remounted in the spectrograph. The values obtained with maximum deviations were

C_{10} (melted sample)	23.03 ± 0.03; 23.04 ± 0.04; 23.00 ± 0.06
C_{11} (melted sample)	25.31 ± 0.03; 25.30 ± 0.03; 25.27 ± 0.04; 25.32 ± 0.03; 25.34 ± 0.03
C_{12} (melted sample)	27.20 ± 0.01; 27.16 ± 0.02; 27.18 ± 0.02
C_{12} (pressed sample)	27.29 ± 0.02; 27.32 ± 0.03
C_{13} (melted)	34.91 ± 0.03; 34.92 ± 0.04
C_{16} (crystallized from acetone)	35.44 ± 0.07; 35.50 ± 0.06
C_{17} (crystallized from acetone)	39.98 ± 0.06; 39.98 ± 0.07
C_{18} (melted)	39.86 ± 0.04; 39.80 ± 0.06
C_{18} (crystallized from acetone)	39.62 ± 0.07; 39.62 ± 0.07
C_{19} (crystallized from acetone)	44.07 ± 0.07; 44.19 ± 0.10

Since the samples were prepared, using essentially the same methods, by two independent workers, samples of C_{12} and C_{13} were used to check the reproducibility of the chemical preparation.

	Sample I	Sample II
C_{12}	27.20 ± 0.01	27.18 ± 0.03; 27.16 ± 0.02
C_{13}	34.91 ± 0.02	34.02 ± 0.01

C_{11} was prepared by two entirely different methods: (1) by hydrogena-

(8) F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.* (London), **A128**, 214 (1930).

tion of undecylenic acid and (2) by the alcohol–bromide–cyanide method from C_{10}. The results were

Hydrogenated Undecylenic	25.32 ± 0.03; 25.34 ± 0.03; 25.31 ± 0.03; 25.30 ± 0.03
Alcohol–Bromide–Cyanide	25.27 ± 0.04

The measurements for an entirely new modification of C_{14} acid are given. For the first five orders (fourth order is too weak for measurement), it is observed sin θ/n = 0.02103 (wk); 0.02103 (com), 0.02102 (wk) and 0.02094 (wk); average 0.02100; d = 36.64 Å.

This new modification of C_{14} was checked by preparing a new pressed sample which gave the value 36.64 Å., the maximum deviation being in both cases 0.05 Å.

Discussion of Results

From the data given it is seen that the results obtained for any one acid by a single method of preparation of the sample, except for the case of the pressed sample of C_{19}, give spacings which check within the experimental error. These results were not only reproducible with the same sample of the acid, but also with different samples of the acid prepared by the same methods by two independent investigators. It was also found in the case of undecylic acid (C_{11}) that the results were reproducible for two entirely different methods of preparation of the acid. This wide range of reproducibility, combined with the increased accuracy, permits the use of the reported substances as useful standards, where long spacings are desired.

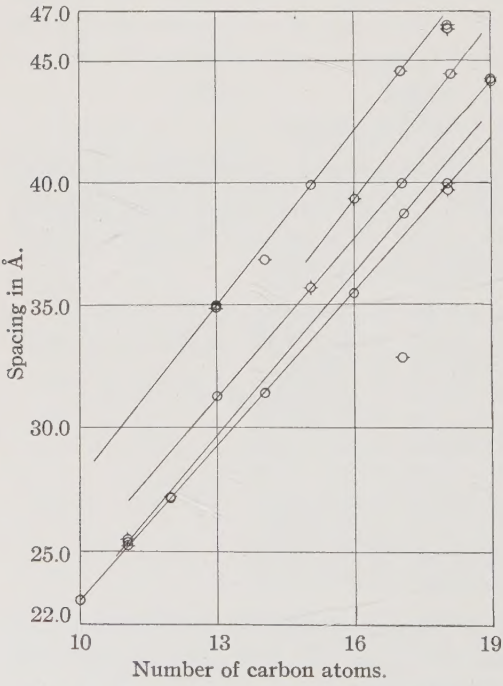


Fig. 1.—Pure acids: ○, melted sample; -○-, pressed sample; -⊙-, sample crystallized from acetone.

In Table I are given our values for the spacings of the pure acids as compared with those obtained by Francis, Piper, and Malkin.[8] In many cases there is a real difference which is sometimes as much as one per cent. In most cases our values are lower than those of Piper.

From the data given it is observed that there are deviations, which appear to be outside of the experimental error, between the spacings obtained for the same modification of a single acid, depending upon the method of preparation of the samples. Piper, Malkin and Austin[9] found similar variations for various long-chain compounds which in some cases were as much as one per cent. Their variations, in the case of fatty acids, were not more than one-half of one per cent., which is comparable with our findings.

If the values obtained from the melted samples and from those crystallized from acetone are compared, it is seen that the lower members of the fatty acid series check very well (except for C_{11}). The higher members (C_{14} and above) deviate giving a value for the melted sample which is higher than the acetone value. A possible explanation for these facts is as follows. The acetone samples were all obtained by evaporating the solutions at room temperature. For these samples the crystallization took place rather slowly, and there were no strains set up due to temperature changes on the solid after it was once formed. The samples crystallized from the melt were formed at their respective setting points, and then cooled to room temperature. In the case of the higher members of the series this crystallization took place very rapidly. The subsequent cooling of these samples gave additional strain, leading to a slightly different tilt of the chains.

The deviations between the pressed sample values and the melted or crystallized from acetone values do not show any regularity. Since these samples were prepared by exerting pressure on the solid acid, it was thought, in analogy to the explanation mentioned above, that the pressure might change the spacing slightly, and thus account for the observed variation. This point is very hard to test because of the difficulty in obtaining equal pressures on all portions of the acid. An attempt was made to test this theory, in the case of C_{19} acid. A pressed sample upon which very little pressure had been exerted gave a spacing of 44.37 Å. A pressed sample upon which much pressure had been exerted gave a spacing of 44.14 Å. This difference seems to be greater than the experimental error in the two measurements. The shift in the spacing is in the right direction, and would seem to substantiate the proposed explanation. This small variation with varying pressure might also be the cause for the decrease in sharpness of the reflections in the case of the pressed samples.

From an inspection of Fig. 1 it is seen that a plot of the spacing obtained against the carbon content of the acids gives a series of straight lines, as has already been known. According to the previous discussion, the spacings obtained from the samples which were crystallized from acetone are the most accurate values. If these spacings are considered, it is seen that the linear dependence with the carbon content is fulfilled, even with the increased accuracy obtained in this work. Also, as has already been

(9) S. H. Piper, T. Malkin and H. E. Austin, *J. Chem. Soc.*, **129**, 2310 (1926).

known, the even and odd acids fall on separate lines. This indicates a different tilt in corresponding even and odd modifications. Malkin[10] has offered a simple explanation for this phenomenon. According to his picture there would also exist in the case of tilted chains a difference in packing of the end links of the chains of even and odd acids. This difference is supposed to account for the alternation in melting points. We find that the C_{11} acid, although belonging to a different line, lies nearly on the line connecting the C_{10} and C_{12} acids. This would indicate practically identical tilt of the chains, provided the end groups were arranged correspondingly. A very decided alternation in the melting points, however, forces us to assume a difference in the arrangement of the end groups.

We have further independent evidence of such a difference in arrangement. We observe that in all the modifications (A, B and C, as far as we could obtain them) of the acids, the even orders of the even acids are relatively stronger than the even ones in the odd series (of course in all these cases the even orders are always of lower intensity than the odd ones, in the range of orders studied by us). Since the relative strength of the orders is a function of the density along the chains, this means that the packing of end groups is different in odd and even cases.

Such difference in packing is further shown in the discovery of a new modification in the case of the C_{14} acid (pressed sample). The spacing of this modification does not seem to fit any previously known modification with sufficient accuracy. The most remarkable difference is, however, to be found in the intensity distribution. It is found: first order, weak; second order, strong; third order, weak; fourth order, indicated; fifth order, weak.

As a rule we observe fewer modifications than Francis, Piper and Malkin[8] with similar treatment. This was true especially of the D modification, which was never found except for C_{17} (pressed), where it was just indicated. It will be seen, in the following paper, that a larger number of modifications is readily obtained in the case of mixtures. In view of the high purity of our acid samples and measurable differences in spacings from other authors, this might suggest differences in composition as an explanation for the above phenomenon.

Summary

The interplanar distances of the (001) planes have been measured for the series of very pure normal fatty acids ranging from C_{10} to C_{19}.

The values thus obtained are of higher accuracy than of any similar previous measurements.

Depending upon the method of preparation of the sample slight variations in the spacings are observed.

The C_{19} acid was prepared as a part of this investigation.

(10) T. Malkin, *Nature*, **127**, 126 (1931); T. Malkin, *J. Chem. Soc.*, 2796 (1931).

An entirely new modification of fatty acids was discovered in the case of the C_{14} acid.

X-RAY STUDIES OF MIXTURES OF FATTY ACIDS[1]

Introduction

x-Ray studies on well-defined mixtures of long chain compounds are relatively few. Most of the results available so far we owe to Piper and his co-workers.[2]

Since we had a series of unusually pure fatty acids available and since we are particularly interested in mixtures of long chain compounds from the standpoint of polymerization, this study was undertaken.

Experimental

I. Two-Component Mixtures of Fatty Acids

1. General. (a) **Preparation of Samples.**—All samples of the mixtures were prepared by the same method. In each case, samples of the acids were weighed out to 0.0001 g. The acids were then fused together in a watch glass and kept just above the melting point for some time. Continual stirring with a small glass rod assured thorough mixing of the several components. The entire mass was then solidified by rapid cooling.

The sample plates were prepared by melting and subsequent solidification of portions of these mixed samples on glass plates. Whenever a check was run on any sample, a second portion of the mixture was taken solidified on a glass plate, and then remounted in the spectrograph. The materials used and the x-ray technique are the same as used in the previous investigation.[3]

(b) **Explanation of Tables.**—Whenever the deviation for a value is listed, it will be the maximum deviation from the mean in Ångström units. Where more than one value is listed for a particular mixture, it is a check on the reproducibility of the result, unless otherwise explained. The final

(1) Emil Ott and F. B. Slagle, compare preliminary note, *J. Phys. Chem.*, **37**, 257 (1933).

(2) Hydrocarbons: S. H. Piper, D. Brown and S. Dyment, *J. Chem. Soc.*, **127**, 2194 (1925); G. L. Clark, *Nature*, **120**, 12 (1927); S. H. Piper, A. C. Chibnall, S. J. Hopkins, A. Pollard, J. A. B. Smith and E. F. Williams, *Biochem. J.*, **25**, 2072 (1931). Acids: S. H. Piper, T. Malkin and H. E. Austin, *J. Chem. Soc.*, **129**, 2310 (1926); also F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.* (London), **A126**, 214 (1930).

(3) F. B. Slagle and Emil Ott, *J. Am. Chem. Soc.*, **55**, 4396 (1933).

column in the graphs represents the best value or values for the spacings of the (001) plane of the mixtures. The composition of all of the mixtures is given in mole percentages.

2. Systems with Components which Are One Carbon Atom Apart.—Mixtures of capric (C_{10}) and undecylic (C_{11}) acids were studied in ten equal steps. In Table I are listed the spacings obtained from these mixtures, and

TABLE I

C_{10}–C_{11} MIXTURES

Mole % C_{10}	Mole % C_{11}	Spacing with dev.	Av. spacing
0.0	100.0	25.32	25.32
10.7	89.3	25.03 ± 0.04	25.03
20.8	79.2	24.69 ± 0.03	24.69
30.2	69.8	24.55 ± 0.02	24.55
41.8	58.2	24.37 ± 0.04 24.39 ± 0.05	24.38
51.8	48.2	24.20 ± 0.01 24.20 ± 0.01	24.20
61.9	38.1	23.71 ± 0.01	23.71
71.4	28.6	23.58 ± 0.01	23.58
81.2	18.8	23.33 ± 0.00	23.33
90.7	9.3	23.19 ± 0.02	23.19
100.0	0.0	23.02	23.02

Typical results on these C_{10}–C_{11} mixtures are as follows: mole % C_{10} = 51.8; mole % C_{11} = 48.2; $\sin \Theta/n$ = 0.03179 (com.), 0.03179, 0.03178 (com.) and 0.03182 (wk); average = 0.03179; d = 24.20 Å.

in graph I their plot is given. Figure 1 shows prints of three of the C_{10}–C_{11} mixtures together with pure C_{10} and pure C_{11}. It is observed that the lines obtained from the mixtures are comparable in sharpness with those obtained from the pure acids, and that each mixture gives a single spacing.

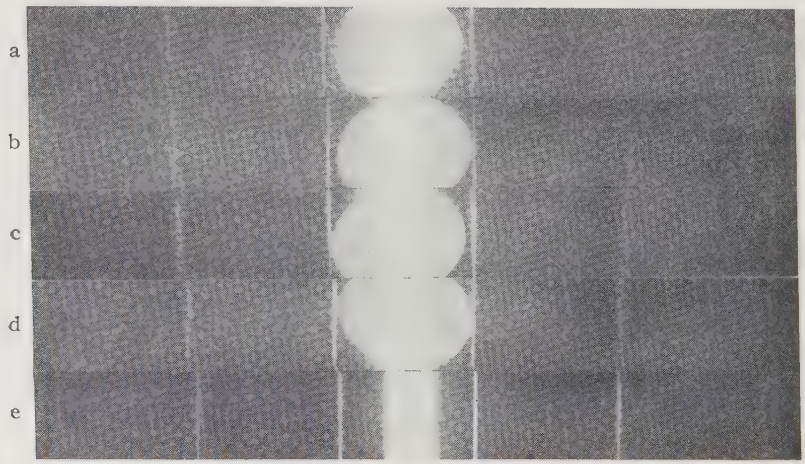


Fig. 1.—C_{10}–C_{11} acid mixtures: a, pure C_{10} acid; b, C_{10} = 81.2%; C_{11} = 18.8%; c, C_{10} = 61.9%; C_{11} = 38.1%; d, C_{10} = 30.2%; C_{11} = 69.8%; e, pure C_{11} acid.

3. Systems with Components which Are Two Carbon Atoms Apart. (a) **C_{10}–C_{12} Acid Mixtures.**—Table II gives the spacings obtained for the various mixtures of C_{10} and C_{12} fatty acids which were studied. It is observed that in the case of two of the mixtures more than one spacing is reported. That these spacings correspond to different modifications for these particular mixtures, and not to phases of different composition, was proved for the mixture of 43.8% of C_{10} and 56.2% of C_{12} as follows. The sample was prepared in the usual manner and a picture taken immediately. Two spacings were observable which were 25.12 Å. and 25.90 Å. The same sample plate was exposed two days later and gave two spacings: 25.08 Å. and 26.92 Å. After a total of two weeks, this sample plate was again exposed and this time just one spacing of 26.92 Å. was observed. Thus the spacing of 25.90 Å. observed on the first picture corresponds to a rather unstable modification which changes over completely to a second modification having a spacing of 26.92 Å. During this change the amount of the remaining modification corresponding to 25.10 Å. (average of 25.12 and 25.08) was practically unchanged, judging from the intensities of the lines. However, upon standing for two weeks it also changed to the modification with the spacing of 26.92 Å.

This same explanation holds for the mixture of C_{10} = 53.4% and C_{12} = 46.6%. Here, however, only two spacings are observed; the modification having the spacing of 26.14 Å. is present in small amounts, and upon standing changes over into a more stable modification which has the spacing of 25.31 Å.

Plots of the spacings obtained for the C_{10}–C_{12} mixtures are given in graph II. Prints of pure C_{10} and of pure C_{12} together with several of the mixtures are given in Fig. 2. Also in Fig. 2 are given prints of the mixture having the composition of 43.8% of C_{10} and 56.2% of C_{12} showing the changes in modification that took place when the sample was allowed to stand over a period of two weeks.

TABLE II

C_{10}–C_{12} MIXTURES

Mole % C_{10}	Mole % C_{12}	Spacing with dev.	Av. spacing
0.0	100.0	27.18	27.18
22.5	77.5	27.10 ± 0.03	27.10
43.8	56.2	25.12; 25.08 ± 0.03; 25.90	25.10
		26.92 ± 0.07; 26.92 ± 0.04	25.90 26.92
53.4	46.6	26.14 ± 0.02; 25.31 ± 0.02	26.14 25.31
63.2	36.8	24.94 ± 0.03	24.94
82.6	17.4	23.53 ± 0.05; 23.54 ± 0.04	23.54
100.0	0.0	23.02	23.02

A typical calculation on these C_{10}–C_{12} mixtures is as follows: mole % C_{10} = 22.5; mole % C_{12} = 77.5; $\sin \theta/n$ = 0.02839 (com.), 0.02839, 0.02836 (com.) and 0.02842; average = 0.02839; d = 27.10 Å.

(b) C_{16}–C_{18} Acid Mixtures.—This work on mixtures of palmitic (C_{16}) and stearic (C_{18}) acids is a repetition of the work reported by Piper, Malkin and Austin[4] on these same two acids, except that the mixtures have slightly different compositions. Each mixture gave a single spacing,

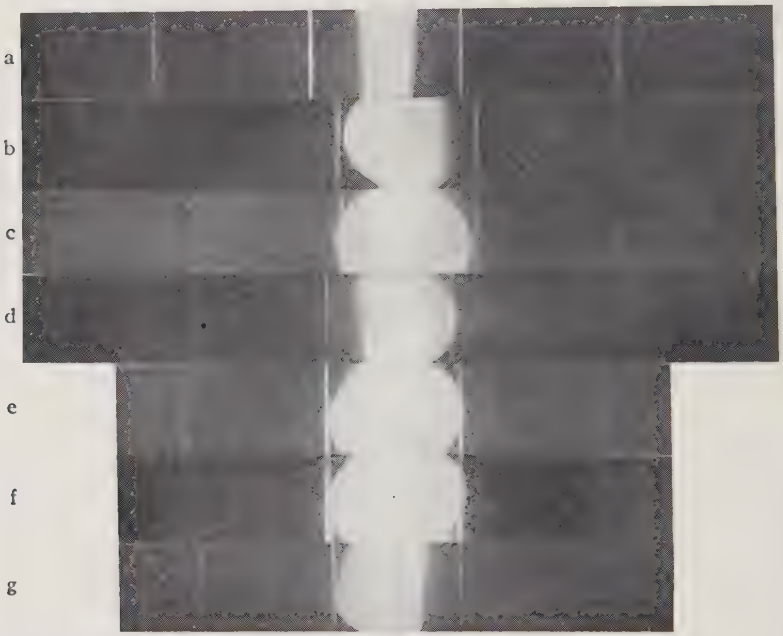


Fig. 2.—C_{10}–C_{12} acid mixtures: a, pure C_{10} acid; b, C_{10} = 63.2%; C_{12} = 36.8%; c, C_{10} = 53.4%; C_{12} = 46.6%; d, pure C_{12} acid. Effect of time on mixture: C_{10} = 43.8%; C_{12} = 56.2%: e, picture taken immediately; f, picture taken after 2 days; g, picture taken after 2 weeks. Sections b and c were placed incorrectly in making the illustration; they should have been reversed in position to match a and d.

the lines for these mixtures being as sharp as those for the pure acids. Table III gives the spacings for the mixtures of C_{16} and C_{18} acids, and graph III gives the plot of these spacings.

TABLE III

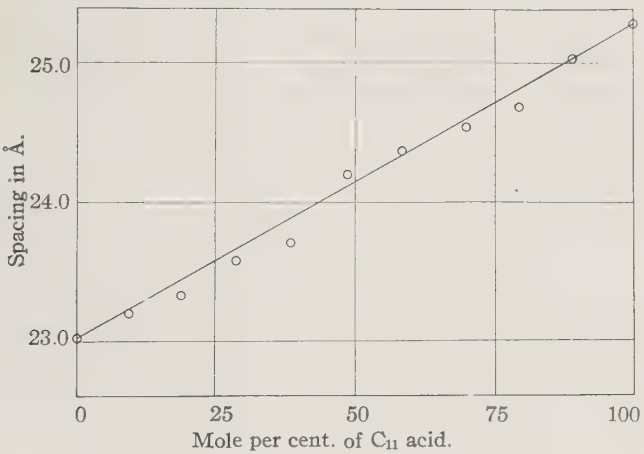
C_{16}–C_{18} MIXTURES

Mole % C_{18}	Mole % C_{16}	Spacing with dev.	Av. spacing
100.0	0.0	39.83	39.83
89.3	10.7	39.72 ± 0.02	39.72
72.8	27.2	39.49 ± 0.04	39.49
47.5	52.5	38.50 ± 0.04	38.50
23.3	76.7	38.14 ± 0.02	38.14
9.3	90.7	35.88 ± 0.04	35.88
0.0	100.0	35.52	35.52

(4) S. H. Piper, T. Malkin and H. E. Austin, *J. Chem. Soc.*, **129**, 2310 (1926).

4. Systems with Components which Are Three Carbon Atoms Apart.—Francis, Piper and Malkin[5] report that combination spacings are obtained for equimolar mixtures of fatty acid chains of n and $n + 1$, n and $n + 2$, and n and $n + 3$ carbon atoms apart, but that equimolar mixtures of chains of n and $n + 4$ carbon atoms apart crystallize separately. They give, however, no data for such mixtures beyond the n and $n + 1$ equimolar mixtures, and fail to say anything about mixtures which are not equimolar.

In our work on mixtures of fatty acids of chain lengths n and $n + 3$ we have studied non-equimolar mixtures as well as equimolar ones. The principal studies were made on mixtures of C_{10} and C_{13} acids. The following results were obtained.



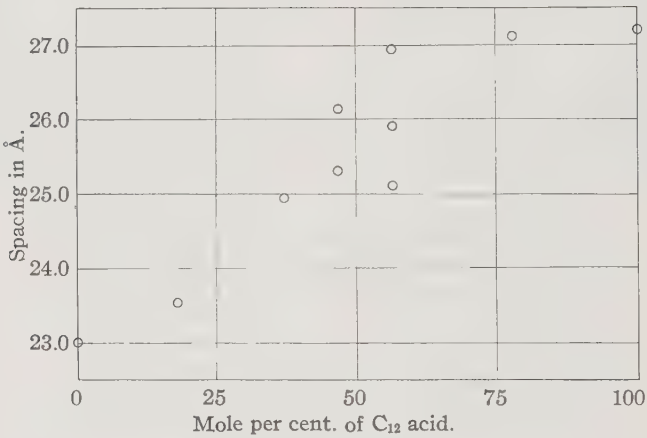
Graph I.—Mixtures of C_{10}–C_{11} acids.

(a) **Equimolar Mixture, Mole % C_{10} = 49.9; Mole % C_{13} = 50.1.**—Two separate sample plates were prepared and exposed. The spacings obtained were 26.30 Å.; 24.21 Å. and 26.29 Å.; 24.18 Å., respectively. The spacing corresponding to 24.20 Å. (average of 24.18 and 24.21) was calculated from a single first order which was very weak. As might be expected the spacing of 26.29 Å. falls on the odd acid curve corresponding to a carbon content of $11^1/_2$ carbon atoms.

(b) **Non-equimolar Mixture, Mole % C_{10} = 24.8; Mole % C_{13} = 75.2.**—Two separate samples of this mixture were prepared and exposed. Film (1) corresponds to the picture obtained from the sample which was crystallized slowly from the melt (approx. one-half minute). Film (2) corresponds to the picture obtained from the sample which was prepared by rapid crystallization from the melt (approx. two seconds). The spacings from the first case are 34.94; 28.87 and 26.36 and from the second case 34.95 and 29.59 Å.

(5) F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.* (London), **A128**, 214 (1930).

From the results obtained here we can see that the speed of crystallization affects the results very markedly. It is seen that the sample which was prepared by slow crystallization from the melt gave three sets of lines, all of which were of equal intensity. The sample which was prepared by rapid crystallization gave only two sets of lines, one set being weak. The set of strong lines on this second film (spacing equal to 34.95 Å.) corresponds exactly to one of the sets of lines found on the first film. The weak set of lines on this second film (spacing equal to 29.59 Å.) does not correspond to any set of lines on the first film. Thus we observe a total of four modifications in these two samples.



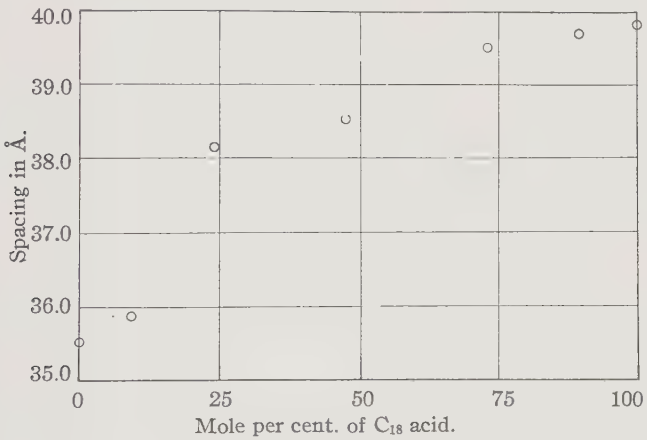
Graph II.—Mixtures of C_{10}–C_{12} acids.

(c) **Non-equimolar Mixture, Mole % C_{10} = 75.5; Mole % C_{13} = 24.5.**—A single picture was taken of the mixture. The calculations gave d = 24.64 Å. Only one set of lines is found for this mixture. The spacing obtained corresponds definitely to a mixed crystal and not to either pure acid.

For any of the three compositions listed above, mixed crystals are present since the spacings observed do not check with the pure acids. In the case of the mixture C_{10} = 75.5% and C_{13} = 24.5%, there is evidently complete mixing since there is only one phase present. In the case of the mixture C_{10} = 24.8% and C_{13} = 75.2%, we obtain a maximum of four phases. These phases represent different modifications and not phases with different composition. This is demonstrated by the fact that upon slow crystallization we obtain three phases, one of which is identical with one of the two phases obtained by rapid cooling; whereas the other is a new phase. Since the spacing corresponding to this common phase is nearly the same as the A modification for pure C_{13} acid, one might think that perhaps C_{13} crystallized out separately, leaving behind a mixture richer in C_{10}. This appears unlikely for two reasons: first, increase of speed of crystallization

ought to hinder the separation of C_{13}; however, the intensity of this spacing on a sample obtained by rapid cooling shows no decrease in intensity. As a matter of fact, we find that the remaining phase (the residual mixture) from the rapidly cooled sample is present in very small amounts. In comparison with the sample with slow cooling, the sample with rapid cooling would appear to show smaller amounts of mixed crystals, which is certainly contrary to any reasonable anticipation. Second, the comparable mixture (C_{10} = 75.5%; C_{13} = 24.5%) shows complete solid solution formation only.

In the equimolar mixture we have either two phases of different composition or two phases of identical composition in different modifications. We favor the latter viewpoint in consideration of the results obtained with other mixtures, such as C_{10}–C_{12}.



Graph III.—Mixtures of C_{16}–C_{18} acids.

In addition to the C_{10}–C_{13} mixtures studied above an equimolar mixture of C_{15} and C_{18} acids (C_{15} = 49.8%; C_{18} = 50.2%) was investigated. The calculations gave spacings of 39.76 and 37.31 Å.

It is seen that this mixture gives two spacings, the values of which lie approximately half-way between the values of the proper modifications of C_{15} and C_{18} pure acids.

5. Systems with Components which Are Four Carbon Atoms Apart.—An equimolar and a non-equimolar mixture of C_{10} and C_{14} acids were used for investigations of mixtures of acids of n and $n + 4$ carbon atoms apart. The results obtained were: (a) two pictures were taken of the equimolar mixture of C_{10} and C_{14} acids (C_{10} = 50.1%; C_{14} = 49.9%). The first picture was taken immediately after the sample plate was prepared (d = 26.98) and the second picture on the same sample after two weeks had elapsed (d = 31.19).

On film (1) there was an indication of a first order (too weak to measure) of another series of lines which would give a longer spacing than the 26.98 Å. which was observed. This longer spacing would in all probability correspond to the spacing calculated from film (2). On film (2) there was not even an indication of a set of lines corresponding to the 26.98 Å. spacing, which means that the transformation to the modification with the longer spacing was complete.

It is of interest to note that according to the average composition (C_{12}) we find the spacing in the first picture close to the C modification of pure C_{12} acid (the only modification observed for this acid). It has been observed in previous cases (C_{10}–C_{12} and C_{10}–C_{13} mixtures) that such mixtures upon standing, or upon variation in speed of solidification, will change modification. In the present case a change of spacing occurs which we would like to interpret in a similar fashion. However, the new spacing observed corresponds closely to the C modification of pure C_{14}. We therefore have to consider the possibility of an unmixing of our sample. Since our original mixture has to be considered as a random arrangement it is hard to imagine that chains possessing considerable length may rearrange to form crystals containing one chain length only. Such a rearrangement, which would involve the moving about of the chains in a relatively regular crystalline arrangement, is quite different from the type of change involved in a change of modification. There, only a variation in tilt is necessary which does not affect, fundamentally, the relative position of the chain-like molecules. This latter possibility can be easily imagined to occur, and experiments show that it does occur. The first possibility appears quite unlikely and the experimental evidence seems to be against it. Namely, since we have an equimolar mixture, the formation of crystals of pure C_{14} only would by necessity give rise to the formation of crystals of pure C_{10}. This C_{10} acid would be crystallized under the conditions of the experiment. In consideration of the smaller size of the C_{10} molecules, these crystals could be formed as readily as those of C_{14}. However, although we find a spacing close to that of pure C_{14}, we find absolutely no trace of spacings that might be associated with any modification of pure C_{10}. Furthermore, if unmixing in the solid would occur, one would not expect it to be complete; so that there would remain lines corresponding to the original mixture (or one similar to it), which is in no way indicated by experimental evidence. Also if the C_{14} acid that might be separated is entirely free of C_{10} acid, the spacing observed is sufficiently different from pure C_{14} acid as to be outside the experimental error. In the still clearer case of C_{14}–C_{18} acid mixture (the data on this mixture are given below) no indication of unmixing was found at all. Thus we feel justified in claiming that the C_{10}–C_{14} mixture does not unmix in the above case, and that the new spacing observed upon standing is a new modification of the

original mixture, which by chance falls close to the C modification (the only modification observed) for pure C_{14}. We have emphasized this point because similar phenomena occur in many binary mixtures of components more than four carbon atoms apart. (b) The non-equimolar mixture of C_{10} and C_{14}(C_{10} = 25.0%; C_{14} = 75.0%) upon exposure gave a picture with just one set of strong lines. There were, however, three very faint first order reflections appearing in addition. The four modifications have the following spacings: 31.27 (strong), 33.88, 28.54 and 26.96. (c) An equimolar mixture of C_{18} and C_{14} (C_{18} = 50.1%; C_{14} = 49.9%) gave the two spacings 39.05 and 35.58 Å.

Since the equimolar mixture of C_{14} and C_{18} acids has a composition equal to pure C_{16} acid, it is of interest to compare the spacings obtained in each case. The spacing of 35.58 Å. corresponds very closely to the C modification of pure C_{16} acid (which value is 35.53 Å.). Only the C modification of pure C_{16} acid was observed by us. Francis, Piper and Malkin,[5] however, report a B modification for pure C_{16} acid with a spacing of 39.1 Å.

6. Systems with Components which Are Five Carbon Atoms Apart.— For the study of mixtures of chains of n and $n + 5$ carbon atoms an equimolar mixture of C_{10} and C_{15} acids was used. Two separate sample plates were prepared and exposed and the results obtained from each are given: mole % C_{10} = 50.1; mole % C_{15} = 49.9; d = 39.62, 35.35; 28.06 and 24.98; d = 39.70, 35.44 and 27.93.

We have four modifications for this equimolar mixture. This makes the interpretation somewhat difficult, especially in view of the fact that two of the spacings correspond closely to the A and B modifications of pure C_{15} acid. In view of our previous discussions we would be inclined to believe that such coincidences are accidental and consider all four phases as different modifications only. Whether this be true or not, it is quite definite that we have at least partial mixed crystal formation, since two of the phases present give a spacing which cannot be brought into agreement with any of the known data on either pure C_{10} or C_{15} acids.

7. Systems with Components which Are Six Carbon Atoms Apart.— Two equimolar mixtures were used for the study of mixtures of chains of n and $n + 6$ carbon atoms. (a) An equimolar mixture of C_{10} and C_{16} acids (C_{10} = 49.9%; C_{16} = 50.1%) gave spacings equal to 35.31 and 29.15 Å.

Here we see that there are two sets of lines observable; the 29.15 Å. value being very close to the value that C_{13} acid would have if it fell on the even acid curve. The value of 35.31 Å. may correspond to the A modification for pure C_{13} acid. This value as found by us was 34.92 Å. Francis, Piper and Malkin[5] report a value for the A modification of pure C_{13} acid of 35.3 Å. However, it is to be noticed that this value (35.31 Å.) is close to the C modification of C_{16} acid. In view of the previous discussion, we would be inclined to believe that this coincidence is accidental, which is

strengthened by the fact that C_{13} acid (which is the average of an equimolar mixture of C_{10} and C_{16} acids) does have a spacing close to this value. At any rate it is quite definite that there exists at least partial solid solution formation, since the other spacing observed (29.15 Å.) does not correspond to any known spacing for pure C_{10} or pure C_{16} acids. Similar results are indicated by the equimolar mixture of C_{12} and C_{18} acids (C_{12} = 49.9%; C_{18} = 50.1%), the spacings of which were d = 33.32, 28.81, 39.41.

Here a total of three phases is observed. Since the spacings of 33.32 Å. and 28.81 Å. cannot be fitted with any known modifications of pure C_{12} or C_{18} acids, we are certain that at least partial solid solution exists. The spacing of 39.41 Å. corresponds closely to the C modification of pure C_{18} acid but it also corresponds closely to the A modification of pure C_{15} acid (the average composition of an equimolar mixture of C_{12} and C_{18} acids), so that in this case the mixed crystal formation may be almost complete.

8. Systems with Components which Are Eight Carbon Atoms Apart.—An equimolar mixture of C_{10} and C_{18} acids (C_{10} = 49.9%; C_{18} = 50.1%) gave the spacings 31.12, 39.62 and 23.14 Å.

Here we observe three phases, two of which may be identical with the spacings of pure C_{10} and pure C_{18} acids. However, there remains a third phase which has a spacing which cannot be brought into accord with any known spacing for pure C_{10} or pure C_{18} acids. It must therefore be a solid solution of C_{10} and C_{18} acids. So here, as in any previous case, we find at least partial mixed crystal formation.

II. Complex Mixtures of Fatty Acids

In view of the fact that mixed crystals were rather easily formed for two component mixtures of acids over a wide range, it seemed to us quite probable that mixed crystals could be formed for mixtures of more than two components. Francis, Piper and Malkin[5] have shown in their interesting paper that for three neighboring acids in the fatty acid series mixed crystals are easily formed and that from such mixtures a single spacing is obtained. They, however, do not extend their experiments to include more complex mixtures. We have extended such experiments to include mixtures of as many as nine components. Four of these complex mixtures were studied.

The samples and sample plates were prepared in the same manner as described for the two-component mixtures. In all of the pictures obtained from these complex mixtures only two orders (first and third) were observable for a particular phase. The lines were somewhat broadened and the time of exposure was longer than for the two-component mixtures.

The results obtained are as follows. (1) An equimolar mixture of the even acids from C_{10} to C_{18} was studied. Three pictures were taken of this sample. The actual composition was: C_{18} = 18.9%; C_{16} = 19.0%;

C_{14} = 19.5%; C_{12} = 20.2%; C_{10} = 22.4%. For the first and third order sin θ/n = 0.01969 (com.) and 0.01962; average = 0.01965; d = 39.15 Å. In another case sin θ/n = 0.01972 (com.) and 0.01963; average = 0.01967; d = 39.11 Å.

Here just a single spacing was observed indicating complete solid solution formation and the check obtained on the two pictures indicates the reproducibility of the results.

This mixture was also studied by depositing the sample on the glass plate by crystallization from an acetone solution of the mixture. The calculations obtained are as follows (again for the first and third order): sin θ/n = 0.01948 (com.) and 0.01940; average = 0.01944; d = 39.57 Å.

This picture gives one main spacing as calculated above. Also there are indicated several weak first orders of other series of lines, which appear as a band, and which correspond to spacings shorter than the one calculated, indicating partial unmixing as to be expected.

(2) An equimolar mixture of the odd acids from C_{11} to C_{17} was studied. Two pictures were taken; one picture from a sample which was prepared by rapid crystallization of the melt and the other from a sample which had slow crystallization. The actual composition of this mixture was: C_{17} = 26.4%; C_{15} = 25.3%; C_{13} = 24.0%; C_{11} = 24.3%.

(a) **Sample Prepared by Rapid Crystallization.**—For first and third order sin θ/n = 0.01951 (com.) and 0.01941; average = 0.01946; d = 39.53 Å.

(b) **Sample Prepared by Slow Crystallization.**—For first and third order sin θ/n = 0.01906 (com.) and 0.01901; average = 0.01903; d = 40.43 Å.; and first order of second modification sin θ = 0.02059; d = 37.36 Å.

In this second example where slow crystallization of the sample was used we see that the sample gave two spacings (the spacing 37.36 Å. being weak and appearing in the first order only), indicating that under these conditions we obtain either two modifications or the mixed crystal formation is not complete whereas in the first case certainly complete solid solution formation is present.

(3) An equimolar mixture of all of the acids from C_{10} to C_{18} inclusive was made up and the x-ray picture taken. The actual composition of this mixture was: C_{18} = 11.1%; C_{17} = 11.1%; C_{16} = 11.3%; C_{15} = 11.3%; C_{14} = 11.3%; C_{13} = 11.3%; C_{12} = 11.1%; C_{11} = 10.8%; C_{10} = 10.7%. From first and third order sin θ/n = 0.01944 (com.) and 0.01945; average = 0.01945; d = 39.55 Å.

Even with a mixture as complex as this one, only one spacing is observable, indicating that the mixed crystal formation must be essentially complete. (4) A non-equimolar mixture of the even fatty acids from C_{10} to C_{18} was studied. This mixture contained a larger percentage of the higher acids.

The actual composition was as follows: C_{18} = 29.8%; C_{16} = 29.2%; C_{14} = 19.6%; C_{12} = 10.4%; C_{10} = 11.0%. From first and third order $\sin \theta/n$ = 0.01949 (com.) and 0.01945; average = 0.01947; d = 39.51 Å.

Discussion of Results

In the interesting paper by Francis, Piper and Malkin[5] the idea was put forward that the x-ray results on equimolar mixtures of fatty acids might best be explained by assuming an arrangement in which a short and a long molecule would form a double molecule. Since double layers of molecules exist in crystals of pure fatty acids, and since always the length associated with such double molecules is measured, such an arrangement would indeed furnish a simple explanation for the fact that the spacing obtained from the mixture is the mean of the spacings of the components (provided that the proper modifications are taken). We have been inclined to consider such an explanation not adequate, since it is hard to anticipate that from a melt of the mixture such a regular arrangement could be obtained upon rapid cooling. Furthermore, since the forces holding various such molecules together in the lattice are about the same, the difference in energy of an ordered and a non-ordered crystal is small.

The experimental test gives the best answer to these questions. The suggested arrangement can only be complete in equimolar mixtures. It is, therefore, of interest to study mixtures of various concentrations. This has been done for the C_{10}–C_{11} mixtures in which it was shown that for any and every composition one definite spacing was obtained, which spacing was characteristic for a particular mixture. When such spacings are plotted against the composition it is found that the points are scattered closely around the straight line connecting the pure acids (graph I). The fact that the equimolar mixture gives the mean spacing of the two components is therefore nothing more than a special case of this more general rule. Obviously the assumption of double molecules, which has occasionally been brought forward by other chemists, is untenable. These mixtures apparently follow the similar law known for inorganic solid solutions which is expressed approximately as Vegard's rule. It is not surprising that the values are relatively widely scattered, since it has become evident in the previous discussion of the pure fatty acids that the spacings are easily affected by various influences. Similar results appear to be present in mixtures of C_{10}–C_{12} and C_{16}–C_{18}; however, in these cases the picture is complicated by the fact that various compositions do not correspond to the same modification. It appears as if two to three modifications were present, so that the points are scattered around two or three lines, one of which connects the spacings of the pure components. Similar results are obtained for the C_{10}–C_{13} mixtures. In this connection attention must be called to a recent paper[6] in which the existence of a transition point for

(6) R. L. Shriner, J. M. Fulton and D. Burks, *J. Am. Chem. Soc.*, **55**, 1494 (1933).

mixtures of palmitic and stearic acid is interpreted as proof for the formation of a compound. Contrary to this view we are inclined to assume a change in modification only.

Francis, Piper and Malkin[5] indicated that solid solution does not exist in binary mixtures in which the chain length difference is more than three carbon atoms. However, we have obtained definite solid solution formation with C_{10} and C_{14} acids in two concentrations and for one concentration of C_{14} and C_{18} acids (no other concentrations were investigated). In the case of five, six and eight carbons apart it was definitely proved that at least partial solution exists in the solid state. Such mixtures had always C_{10} acid as one component, thus giving a relatively high percentage difference in chain length.

It is of interest to note that the mixtures appear to occur in a larger number of modifications than has been observed for the pure acids in this investigation.

It is a remarkable fact that for any one of the complex mixtures listed in the experimental part, a definite single spacing characteristic for one phase can be obtained. Since one phase only is obtained, this must mean that complete solid solution is present in these cases.

It is likely that the modification present in such mixtures corresponds to the one present in certain binary mixtures with large separation of chain length, namely, the ones which give the longest spacing. This may be surmised from the fact that in the case of these complex mixtures the spacing lies close to the one of the longest component. However, it must be emphasized again that this similarity of spacing cannot mean that the highest component has crystallized out, since definitely no other spacings are present in the proper samples.

In the sample which has been obtained from solution a partial separation has been observed. The spacing is slightly longer than the one obtained from the corresponding melt. Assuming identical modifications, this would mean that the main component contains more of the longer chains than would be given by the average composition, which again would necessitate the presence of phases with a higher content of the lower chains. Actually the main spacing is accompanied by a narrow weak band which must have been produced by various slightly shorter spacings.

The fact that such complex but well-defined mixtures of fatty acids give rise to well-defined reflections from the (001) plane, which interplanar distance must be associated with the chain length (although in the case of the fatty acids, due to the unknown tilt of the chains, the average chain length cannot be definitely calculated), is of special interest, since in previous investigations such an effect was claimed not to exist. Hengstenberg[7] was unable to obtain any spacings associated with the chain length

(7) J. Hengstenberg, *Z. Krist.*, **67**, 538 (1928).

in a complex hydrocarbon mixture (the average length is not given in the reference, but judging from the title the paraffin mixture may be assumed to be C_{60}–C_{80}).

It might be argued that the average chain length was too high to be observable. With our apparatus, depending on the third order which is sufficiently strongly observed in our mixtures, we could measure spacings for a hydrocarbon mixture of average chain length of about C_{100}. It might be objected that the results obtained on the fatty acids are not applicable to other long-chain compounds. For this reason other series are being investigated. At present the preliminary results are available on several series, for which Dr. D. A. Wilson[8] observes the same effect. Since such perfect miscibility is observed for relatively short chain lengths, where the relative length differences of neighbors play a much larger role, it is reasonable to expect similar miscibility for longer chain lengths. Unfortunately such longer acids were not at our disposal in sufficiently pure form that the experimental test could be performed.

The results obtained on the mixtures of the acids are entirely nonambiguous in their interpretation. The lines obtained are surprisingly sharp although less sharp than those obtained on the pure acids or simple mixtures. The falling off of intensities with the higher orders appears to be more rapid than in the case of the pure acids. Since these findings are so much in opposition to the prevailing opinion[9] it seems of interest to make theoretical calculations on such mixtures. This has been done by Dr. M. L. Huggins[10] in this Laboratory. His results are in perfect agreement with our experimental data.

The results obtained seem to us to be of special interest in connection with the structure of high polymers. Some such polymers are assumed to consist of chains of various lengths. If the average chain length is not excessively long, spacings connected with this average chain length should be obtained by the methods used in this work. Such effects have not been previously observed, and this has been used thus far by other workers as a criterion for the presence of chains of varying length. There is only one dissenting paper[11] in which reflections were obtained from polymer formaldehydes which were considered as lower orders of the (001) plane; since the chains are vertical to the (001) plane, the average chain length could be calculated from the data. However, at the time instead of using the concept of average chain length it seemed more cautious to consider the crystals as built up of molecules of essentially the same length only, in agreement with the prevailing opinion. Since it was more likely from chemical considerations to assume varying chain length in polymer form-

(8) Dissertation, the Johns Hopkins University, 1933.

(9) K. H. Meyer and H. Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akademische Verlagsgesellschaft, Leipzig, 1930, pp. 44–45.

(10) Huggins, to be published shortly.

(11) Emil Ott, *Z. physik. Chem.*, **B9**, 378 (1930).

aldehydes, Sauter[12] attacks the existence of "inner" reflections (lower orders of the (001) plane) observed by Ott. In consideration of the results obtained in this thesis, there appears to be every reason to anticipate results such as obtained by Ott on polymer formaldehydes, since the spacings observed lie in a range suitable for observation.

Summary

1. A large number of two-component mixtures of the normal fatty acids C_{10} to C_{18} have been studied. The chain length difference of the two components varied from one to eight carbon atoms. The mixtures with difference in chain length up to three carbon atoms were studied for various concentrations. In all cases mixed crystal formation was established.

2. Very complex mixtures of fatty acids (containing as many as nine components) were also measured and the existence of solid solution demonstrated.

3. These results are discussed in connection with their chemical significance.

(12) E. Sauter, *Z. physik. Chem.*, **B18**, 417 (1932).

BIOGRAPHY

Fred B. Slagle was born near Woodbine, Maryland, on August 17, 1909, the son of Mr. and Mrs. Fulton R. Slagle. He received his public, grammar and high school training in the schools of Maryland. He graduated from Lisbon High School at Lisbon, Maryland in June, 1926 and entered the Engineering School of The Johns Hopkins University in October, 1926. In June, 1930 he was awarded the degree of Bachelor of Science in Chemistry from the Engineering School of The Johns Hopkins University.

He has been a graduate student in the Department of Chemistry of The Johns Hopkins University for the three years, 1930–1933. During the year 1930–1931 he held a University Scholarship and during the two years; 1931–1932 and 1932–1933 he was a student assistant in the Chemistry Department.